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FULLERIDES

Superconductivity at the limit

The successful synthesis of highly crystalline Cs_3C_{60} , exhibiting superconductivity up to a record temperature for fullerides of 38 K, demonstrates a powerful synthetic route for investigating the origin of superconductivity in this class of materials.

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Since the discovery in 1991 of superconductivity in doped C_{60} fullerides¹, these materials have been considered to be a classical example of superconductors in which the electrons couple in pairs due to electron–phonon interactions, as described by the BCS (Bardeen, Cooper and Schrieffer) theory. The BCS theory provides analytical relationships between the transition temperature T_c (below which the material is in the superconducting state), the density of states of the electrons, and the vibrational modes. This allowed the synthesis of new phases with higher values of T_c , so that within a year T_c almost doubled from 18 K to 33 K by simply using larger alkali ions as dopants². However, after this initial burst of activity, progress in C_{60} superconductivity came to a virtual standstill, both experimentally and theoretically. On page 367 of this issue, Alexey Ganin and co-workers report³

a new synthetic approach that allows controlled synthesis of high-quality, highly crystalline Cs_3C_{60} , which, under pressure, turns superconducting at temperatures of up to 38 K.

Superconductivity is one of the most widely studied phenomena in solid-state physics. Even before the discovery in 1986 of the high- T_c cuprate superconductors⁴, superconductivity was a rich field of research, not only for the fascinating perspective of dissipation-free electrical transport, but also because describing the phenomenon involves various aspects of condensed-matter physics. From the perspective of materials science, superconductivity has been challenging because values of T_c predicted by theory for certain materials are usually difficult to obtain experimentally. Until the mid 1980s the highest reported T_c was 23 K for Nb_3Ge , which was considered the limit for conventional superconductors. This intermetallic compound is based on a body-centred-cubic packing of Ge with Nb–Nb pairs on the faces of the cubes, known as the A15 crystal structure. The field has since broadened enormously due to the discovery of novel materials with

strong electron–electron interactions, the heavy-fermion superconductors⁵ and more complex materials (for example, MgB_2 with $T_c \sim 39$ K, ref. 6). Recently, materials with electronic coupling mechanisms that involve magnetic interactions (cuprates with $T_c \sim 100$ K; cobaltates with $T_c \sim 5$ K, ref. 7) and even ferromagnetic interactions (intermetallics such as UGe_2 , $T_c \sim 1$ K, ref. 8) have attracted considerable attention.

Molecular superconductors were discovered in 1980 in a one-dimensional material when hydrostatic pressure was applied, with $T_c = 0.9$ K at 12 kbar (ref. 9). In the following years T_c was pushed to 13 K in two-dimensional molecular conductors. After methods to produce macroscopic amounts of C_{60} had been developed, metallic behaviour was soon induced by doping with alkali metals, followed by the realization of superconductivity at 18 K in 1991 (ref. 1). Within one year an influential paper appeared that provided the theoretical framework for C_{60} superconductivity¹⁰. This theory explained superconductivity as originating from a conventional electron–phonon coupling mechanism, limiting T_c to ~ 30 K. After this value had been attained experimentally², the subject was considered solved, even though important questions remained regarding the physical mechanism of the superconductivity. For example, different spectroscopic techniques indicated that different phonon modes were responsible for the electron pairing. Moreover, few materials allowed detailed studies near the metal–insulator transition.

The work by Ganin and co-authors provides insight into various aspects of the physics of intercalated C_{60} compounds. This research has been hampered by the quality of the samples. In the 1990s, the Meissner effect — expulsion of the magnetic flux and an essential feature of superconductors — corresponded to typically 1% of the sample volume. Conventionally, samples are grown by solid-state reactions and less often by solution in liquid ammonia. Both methods result in granular materials. The synthetic

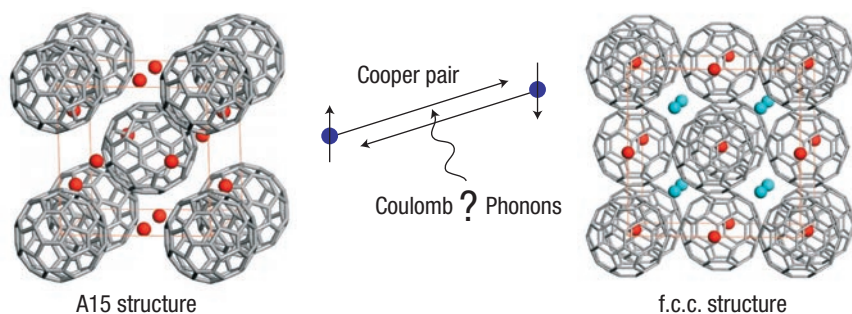


Figure 1 Superconductivity and structure of Cs_3C_{60} . The samples grown by Ganin *et al.* show predominantly the A15 crystal structure (left) and smaller amounts of the f.c.c. phase (right). The differently coloured spheres indicate Cs ions on different crystallographic sites. Superconductivity in the f.c.c. phase is conventionally associated with electron–phonon-mediated pairing. The continuous change through a maximum T_c of 38 K in the A15 phase with hydrostatic pressure shows that electron–electron (Coulomb) interactions are important in this regime near the metal–insulator transition. The straight arrows indicate electron motion; the wavy arrows the pairing interaction.

technique reported by Ganin *et al.* uses methylamine as a solvent and yields Meissner fractions close to 70%. This enables these materials to be studied in much more detail, both crystallographically and electronically.

Another aspect is the difficulty in tuning the electronic properties. This has thus far proved difficult because the intercalated phases are often line compounds, which allow little variation in stoichiometry. Even simple experiments, such as proving that T_c was maximum for C_{60}^{3-} in the face-centred-cubic (f.c.c.) crystal structure¹¹ was difficult. The present work uses hydrostatic pressure as a powerful technique, well known for organic conductors, to modulate electronic properties close to an insulator–metal transition, without affecting the crystal symmetry.

The measurements by Ganin and co-authors indicate that hydrostatic pressure can tune the properties continuously through a maximum value for T_c , without any sign of a first-order transition, as would be expected for an insulator-to-metal transition. The highest values for T_c observed so far were for compounds with an f.c.c. A_3C_{60} crystal structure, where the alkali metal ions (A) occupy the voids between the densely packed C_{60} molecules. It is commonly believed that the degeneracy of the t_{1u} valence band, only present in f.c.c. compounds, is a requirement for the high density of states at the Fermi level, and

therefore superconductivity. Small alkali ions result in a simple cubic packing with low T_c . Ions with a large radius result in tetragonal/orthorhombic distortions or different packings, often rendering a Mott insulator. For example, $NH_4K_3C_{60}$ is a tetragonally distorted insulator at ambient pressure, which can only be turned superconducting by applying pressure with $T_c = 28$ K (ref. 12). Intercalation of C_{60} with the larger Ba^{2+} ion results in Ba_3C_{60} , which also adopts the A15 crystal structure¹³. Our early work on Cs_3C_{60} also identified a two-phase mixture of the A15 and a body-centred tetragonal phase with a T_c near 40 K, but the superconducting phase fractions were very small¹⁴. The synthesis of Ganin *et al.* yields high-quality compounds with large superconducting phase fractions of predominantly the A15 structure and small amounts of the tetragonal phase and the f.c.c. Cs_3C_{60} phase (Fig. 1). The A15 structure seems ideally suited to probe the vicinity of the insulator–metal transition.

Although little research has been performed on C_{60} superconductivity in recent years, the field of molecular electronics has made enormous progress. Progress in synthetic techniques and device fabrication has led to materials in which the electrical conduction is no longer limited by defects such as grain boundaries and impurities. Many experiments now take place in clean-room facilities to minimize the effect of impurities on crystalline devices. Materials research has adopted methods

derived from silicon technology. Interfaces between molecular conductors can now be fabricated to yield field-effect transistors with mobilities that correspond to delocalized charge carriers¹⁵. Gate barriers are nowadays of high enough quality that gate-induced metallic behaviour in organic or inorganic compounds has become feasible. Similarly, it seems natural that the synthesis of high-quality doped C_{60} compounds reported by Ganin *et al.* will allow detailed investigation of the physics of these compounds near the metal–insulator transition. Finally, the various spectroscopic techniques that have provided essential information in the field of the cuprates, joined with the possibility of synthesizing high-quality C_{60} compounds, could take our understanding of superconductivity in these materials to the next level.

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INFORMATION STORAGE

Around the phase-change cycle

The systematic development of phase-change materials has been hampered by experimental and computational difficulties. The first successful modelling of the full phase-change cycle therefore closes an important gap.

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Numerous materials can undergo phase transformations under the action of external stimuli but just one particular group of materials is now generally referred to as ‘phase-change

materials’. The term is commonly reserved for tellurium-based compounds, most often Ge–Sb–Te alloys (GST). Phase-change materials have seen widespread commercialization in data-storage applications, which started in the early 1990s when Matsushita introduced the digital versatile disk random-access memory (DVD-RAM; Fig. 1). The interest in these materials has been intensified as they offer much better scalability and faster switching speed than the currently popular

flash memory and are likely to replace the latter in the near future. In addition, phase-change materials are at the heart of a new generation of optical disks, the so-called super-resolution near-field structure (super-RENS) disks¹. Despite all these technological advances, not much is known about the mechanism of phase change that would allow the design of improved phase-change materials. On page 399 of this issue, Jozsef Hegedüs and Stephen Elliott now report that they have successfully